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THE STATE UNIVERSITY OF NEW JERSEY

Engineering Ceramic Nanophosphors for Optical Applications

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- US Coast Guard
- US Army
- USR Optonex
- Dupont

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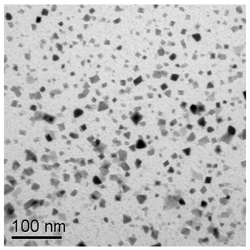
Core Efforts of Research Team

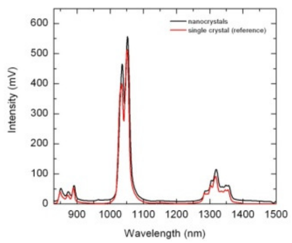
- Low-cost, scalable synthesis of phosphors using solution chemistry
- Systematic study and characterization of physical, chemical and optical properties
- Engineer surfaces and bulk properties of materials for devices
- Theoretical simulation and computation for design of novel dopant and codopant schemes to improve optical efficiency and enable unique emission properties

Current Research

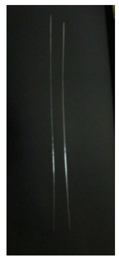
Forms of Materials

Nanoparticles



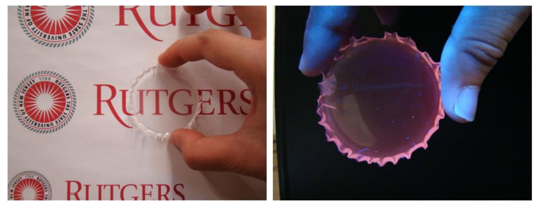


Optical Fibers

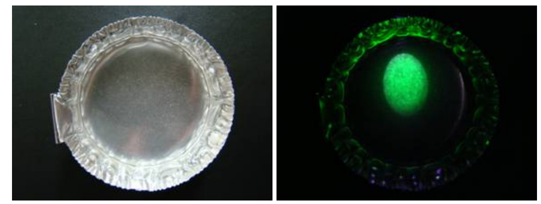


Transparent Polymer Composite Coatings

Downconverting Composites

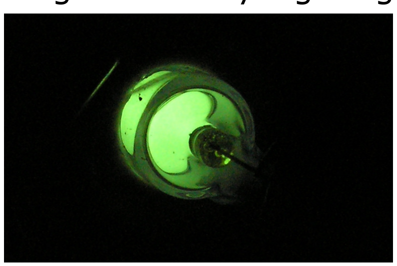


Upconverting Composites

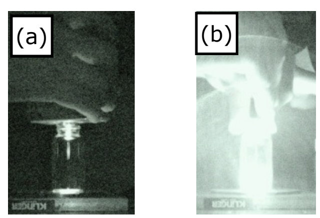


Applications

High Efficiency Lighting

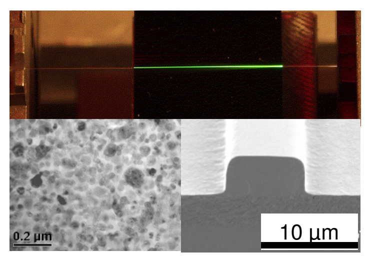


Night Vision Imaging

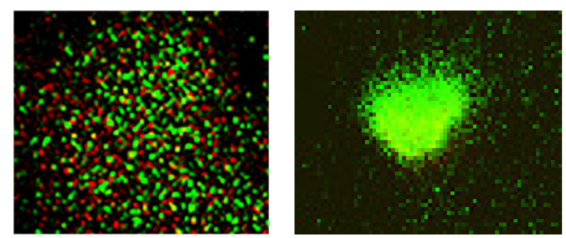


(a) Background (empty vial)
(b) Powder emission using handheld laser

Telecommunication



Biomedical Applications



Images taken using confocal microscope

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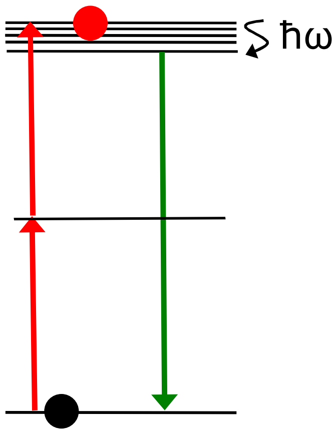
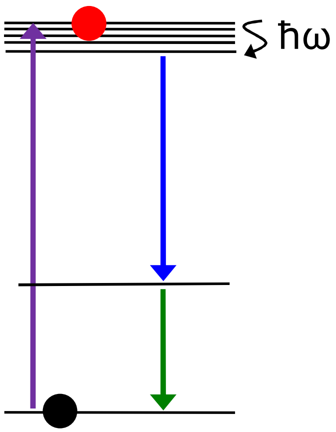
Types of Phosphors

- Classification based on energy conversion
- Up-conversion phosphors
  - emission of high energy photons upon excitation with low energy photon source
    - ❑ maximum quantum efficiency ~ 100 %



- Down-conversion phosphors
  - emission of low energy photons upon excitation with high energy photon source
    - ❑ maximum quantum efficiency ~ 100 %
  - quantum cutting down-conversion: 1 vacuum ultraviolet photon (λ<200 nm) absorbed, 2 visible photons emitted
    - ❑ maximum quantum efficiency ~ 200 %



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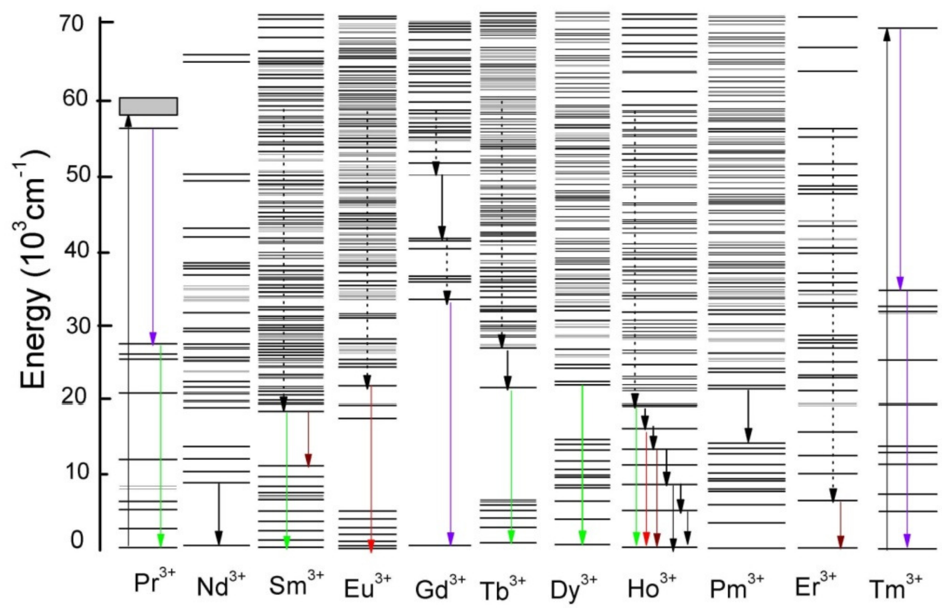
Optical Properties of Phosphors

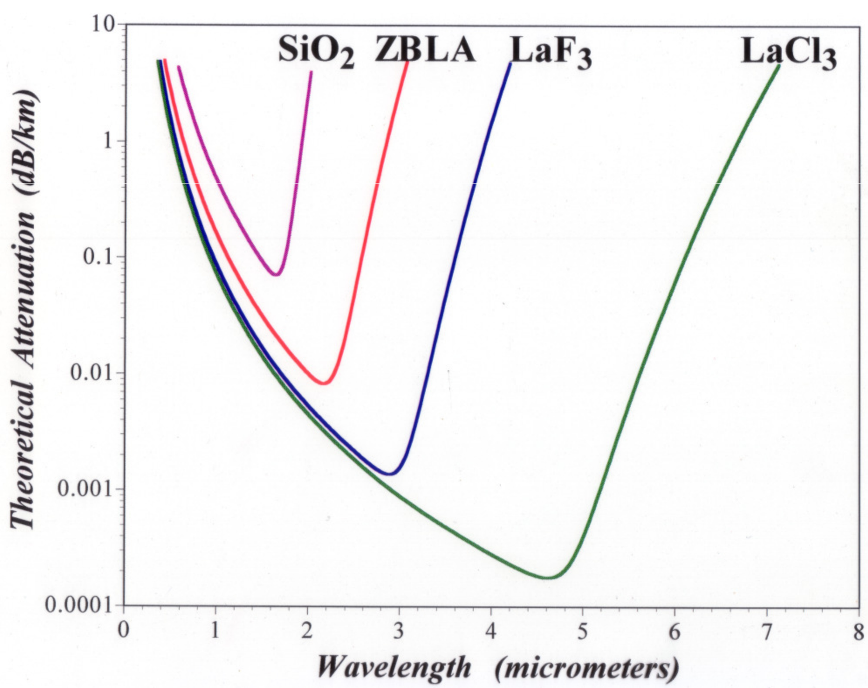
- Properties controlled by:
  - Dopant
    - ❑ radiative transitions predicted from electronic energy levels
  - Host lattice contributions
    - ❑ non-radiative losses, phonon energy, bond ionic character, symmetry of dopant site

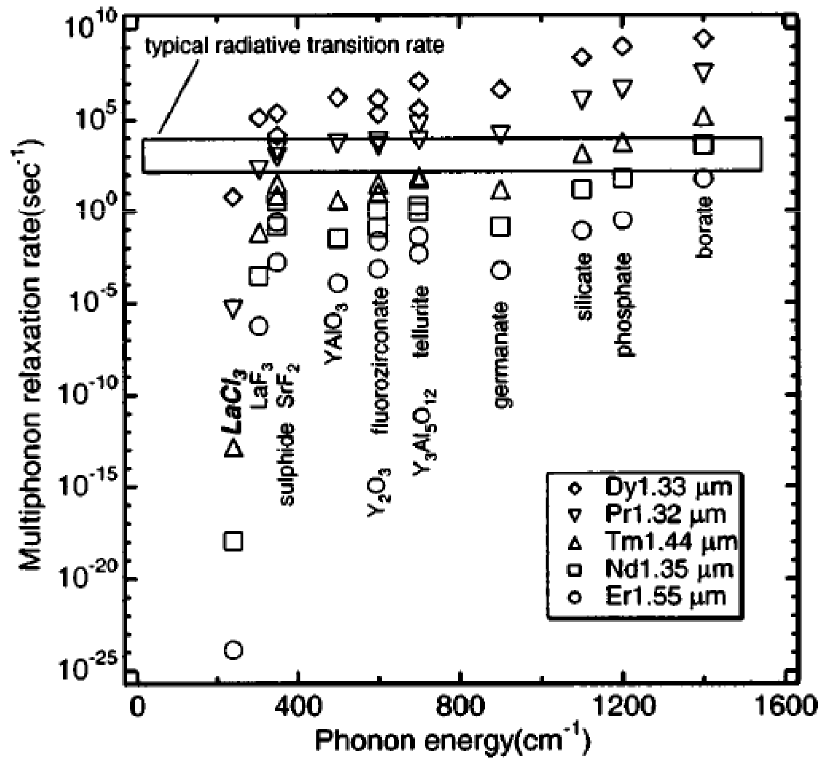


- Desired properties
  - High absorption cross-section at exciting wavelength
  - High fluorescence decay time and emission cross-section
  - High quantum yield
  - High optical transparency in the emitting region
  - Low cost of production, non-toxic, high stability

Why Rare-Earth Doped Halides?

- Low phonon energy host
- Minimize non-radiative losses





K Soga, W Wang, RE Riman, JB Brown, KR Mikeska, J. Appl. Phys. 93:2946 (2003).

Heavy Metal Fluoride Glass Formation

Material	T_g (°C)	T_{crys} (°C)	α (1×10^{-6}) (°C)
ZBLA	310	380	16
ZBLAN	260	360	17

- ZBLA and ZBLAN have better fiber drawing ability than other fluoride glasses
- Difficulties using conventional melt quenching method
  - Moisture sensitivity of precursors and liquid melt
    - ❑ ZrF_4 films were hygroscopic and contained other emission quenching contaminants like reduced Zr and oxide species
  - Segregation due to different vapor pressures of precursors
  - Glass stability - small difference in T_g and T_{crys}
    - ❑ high tendency for formation of crystalline regions
  - Low viscosity and coefficient of thermal expansion

Sol-Gel Synthesis of Halide Glasses

- Limitations of Conventional Processing
  - CVD: segregation problems due to different vapor pressures of component precursors
  - Melt: impurities and crystallization problems

- Advantages of Sol-Gel
  - Purity: purified alkoxide and oranometallic precursors
  - Homogeneity: atomic scale mixing
  - Glass Stability: viscous sintering at low T
  - Compositional Versatility: Cations (Rare earths);
Anions (F, Cl, Br…)
  - Forms: Amenable to fibers, films and bulk optics

J Ballato, M Dejneka, RE Riman, E Snitzer, W. Zhou, J Mater. Res. 11:841 (1996).

Schematic of Sol-Gel Synthesis

Molecular Complex
Synthesis and Characterization

↓

Hydrolysis and Polymerization
Water:Hydrous oxide of component cations

↓

Fluorination

Solid State	Solution Processing	Reactive Atmosphere
Ammonium Bifluoride	Aq. HF in EtOH	Anhydrous HF
200-300°C	120°C	200-300°C

↓

Sintering
Compaction
Densification

Melting
SF_6 or NF_3
800°C

M Dejneka, RE Riman, E Snitzer, J Amer. Ceram. Soc., 76:3147 (1993).

Sol-Gel Precursor Selection

- Metal organic precursors cause undersirable properties
  - "Foam" pellets and films on sintering
  - Optical blackening from residual free carbon
- To overcome drawbacks of metal organic precursors
  - Fluorinating/oxidizing atmospheres
  - Use inorganic precursors

Samples	Wt% C	Wt% H
Hydrous oxide gel – 50°C	22.67	3.69
Solution Fluorination		
Fluorinated – 120°C, 1h	1.74	0.79
Vapor Phase Fluorination		
Anhydrous HF – 200°C	0.23	0.12
Melt Processing		
HF 200 → SF_6 800°C	0.00	0.00

Temp. (°C)	Lifetime (ms)			
	ZHC N_2	ZHC HF	ZBLA N_2	ZBLA HF
100	0.73	1.12	0.38	0.70
200	0.68	1.57	0.47	0.81
300	0.44	2.19	0.48	0.80
325	0.40	2.15	0.49	0.96
400	0.26	2.75	0.34	1
600	0.24		black	black
800	0.18	3.80	black	4.73

M Dejneka, RE Riman, E Snitzer, J Amer. Ceram. Soc., 76:3147 (1993).

Alternative Rare-Earth Systems?

Rare Earth Doped Glasses

Limitations:
- High purity raw materials
- Compositional uniformity
- Crystallization
- High cost of processing
- Limited processability

Rare-Earth Doped Polymer Systems

- dissolve rare-earth ions in polymers

Nanostructured Photonic Composites

- dispersion of rare-earth doped nanocrystals in polymers

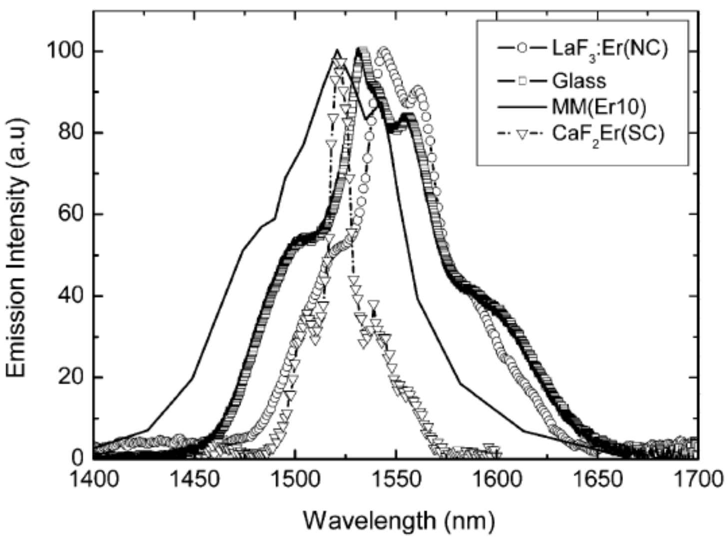
Rare-Earth Doped Polymer Systems

- Advantages of polymer systems
  - Lower processing costs
  - Excellent processability
  - Tunable optical performance with incorporation of multiple rare-earth systems
  - Low weight, flexible

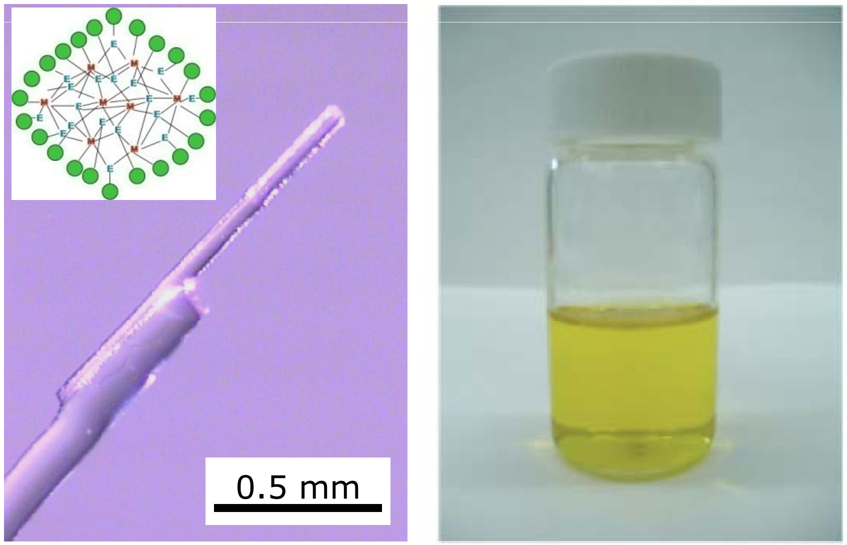
- Limitations
  - Low solubility of rare earth ions
  - Quenching of emission from rare earth ions due to polymer functional groups (e.g. -OH and –CH)

Molecular Minerals

- Inorganic clusters with high solubility in polymers
- Surrounding ligands protect rare earth ions to reduce non-radiative losses and quenching
- Stability issues of inorganic clusters led to development of inorganic nanoparticle-polymer composites



Comparison of IR emission spectrum of Er10 molecular minerals with other Er-doped systems



$(THF)_3Er(SePh)_3$ Molecular Minerals Single Crystals and Solutions

RE Riman, GA Kumar, S Banerjee, JG Brennan, J Amer. Ceram. Soc., 89:1809 (2006).

Alternative Rare-Earth Systems?

Rare Earth Doped Glasses

Limitations:
- High purity raw materials
- Compositional uniformity
- Crystallization
- High cost of processing
- Limited processability

Rare-Earth Doped Polymer Systems

- poor chemical and thermal stability

Nanostructured Photonic Composites

- dispersion of rare-earth doped nanocrystals in polymers

Nanostructured Photonic Composites

- Dispersion of rare-earth doped nanoparticles in IR-transparent polymer matrix
- Combine advantages of polymers and inorganic host
  - inorganic host: low phonon energy, intense emissions, good chemical resistance and high thermal stability
  - polymers: low weight, flexibility, good impact resistance and excellent processability
- Desired properties
  - High optical transparency (low scattering and absorption)
  - High solids loading $\rightarrow$ bright devices
- Suitable for device integration
  - LEDs
  - optical fibers
  - optical waveguides

Hydrothermal Synthesis of Phosphors

- Reproducible with control of particle phase and size
- Versatile and applicable to various material systems
- Low-cost and easy to scale-up

rare earth precursors dissolved in aq. soln.

↓ dropwise

base + solvent
(e.g. NH_4F + water)

↓

hydrothermal reaction
(e.g. heat at 200°C for 2 h)

↓

particle separation or modification for downstream processing (e.g. heat treat)

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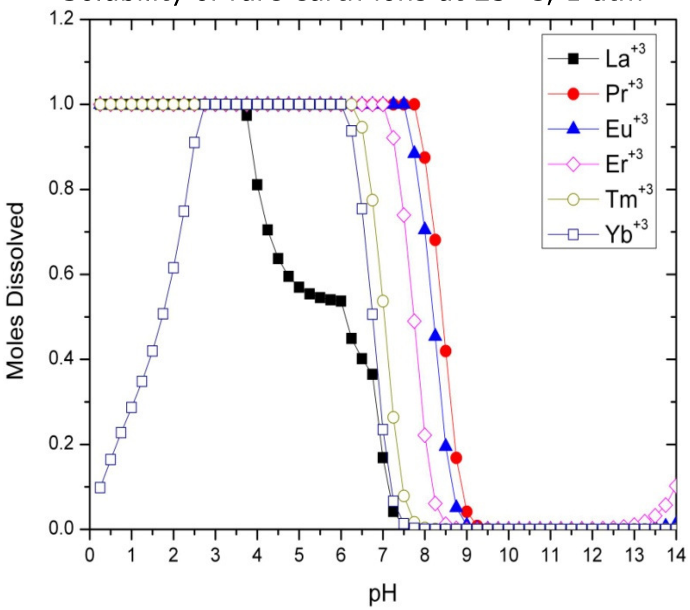
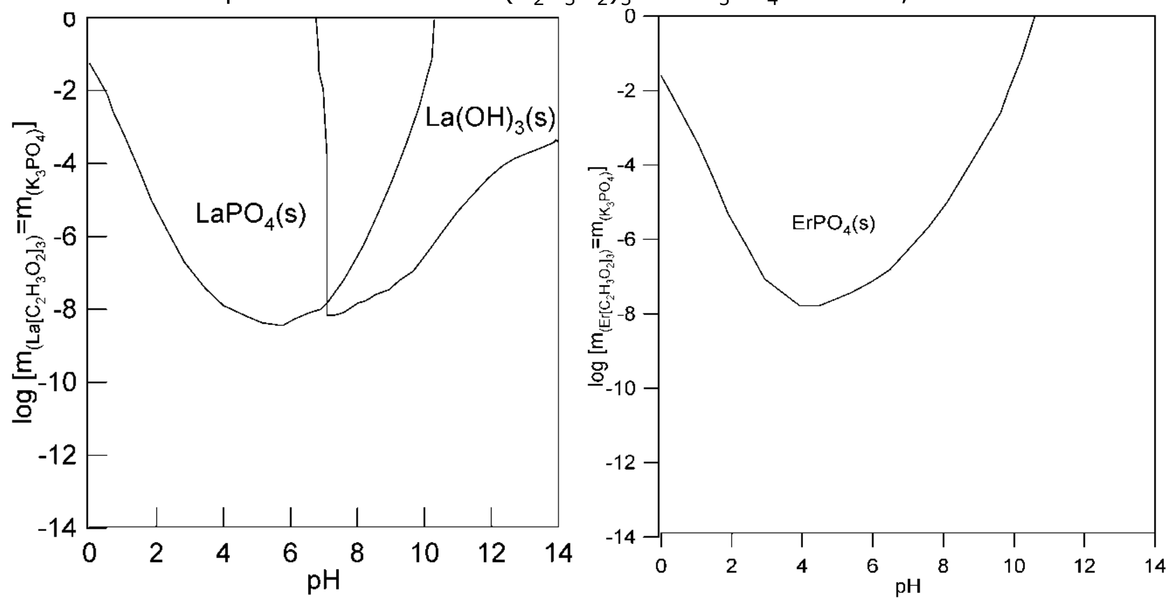
Thermochemical Engineering and Design

- Tool for solvothermal reaction design
- Phase pure products from simulated equilibrium yield diagrams
- Analyze dopant incorporation into host lattice and crystal growth problems

Solubility of rare earth ions at 25 °C, 1 atm

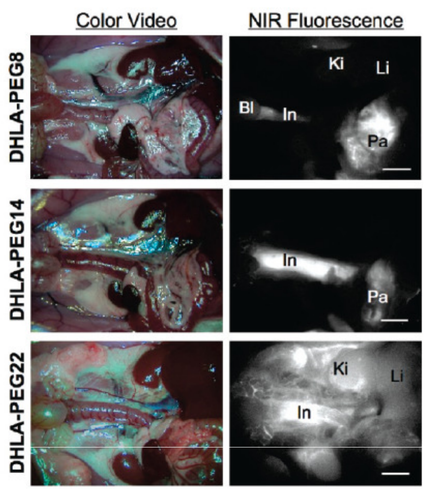


Aqueous solution of $La(C_2H_3O_2)_3$ and K_3PO_4 at 200°C, 25 atm

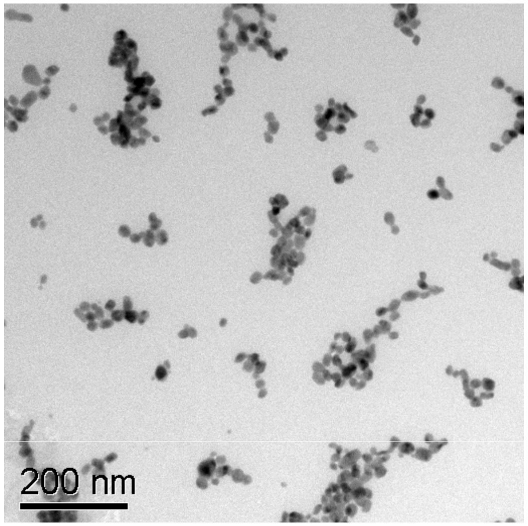


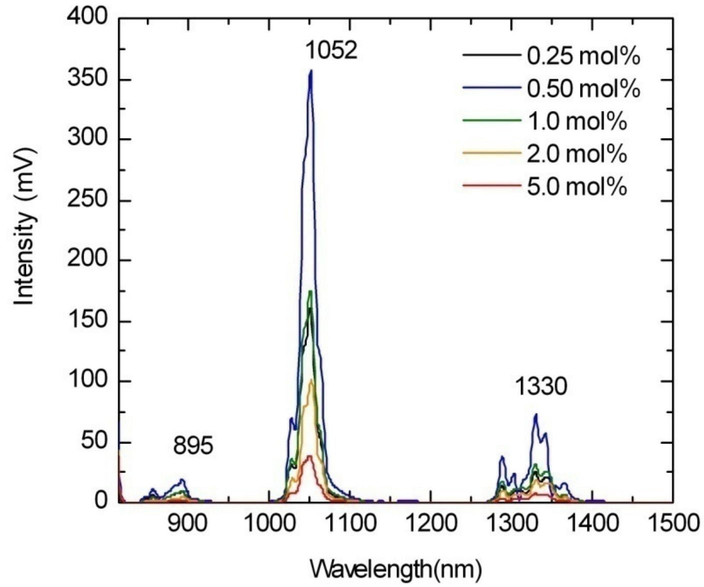
T Andelman, MC Tan, RE Riman, Mater. Res. Innov., *in press*.

IR-emitting YF_3:Nd nanoparticles



HS Choi et al. Nano Lett., *in press*.





- Emerging application in diagnosis and imaging
  - low tissue-penetrating visible emission from conventional fluorescent probes inadequate for deep tissue imaging
  - imaging sensitivity potentially improve by ≥ tenfold
- NIR-emitting rare earth doped phosphors
  - narrow excitation and emission bandwidth
  - tunable over longer NIR range

MC Tan, GA Kumar, RE Riman, J. Appl. Phys., *in press*.

Radiative Properties of YF_3:Nd

- Energy level calculations from Hamiltonian equation
  - $H = H_{FI} + H_{CF}$, where H_{FI} and H_{CF} is the free ion and crystal field contributions, respectively
- Judd-Ofelt intensity parameters, Ω_t (t=2,4 and 6)
  - strength and nature of crystal field acting on rare-earth ion
  - $\Omega_2 = 0.87\times10^{-20}$ cm^2, $\Omega_4 = 1.56\times10^{-20}$ cm^2 and $\Omega_6 = 3.53\times10^{-20}$ cm^2
    - $\Omega_4 > \Omega_6$ to maximize intensity of $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition (i.e. 895 nm)
    - $\Omega_4 < \Omega_6$ to maximize intensity all other transitions from $^4F_{3/2}$ (e.g. 1052 nm)
    - Ω_4/Ω_6 (YF_3:Nd) = 0.44 compared with Ω_4/Ω_6 (YAG:Nd) = 0.54
  - calculate theoretical oscillator strength for any $J \rightarrow J'$ transition

$$\text{oscillator strength, } f = \frac{2m\overline{\omega}_o}{3\hbar(2J+1)} \times \sum_{t=2,4,6} \Omega_t \times \left|\left\langle \alpha J \left\| U^{(t)} \right\| \alpha' J' \right\rangle\right|^2$$

where $\left|\left\langle \alpha J \left\| U^{(t)} \right\| \alpha' J' \right\rangle\right|$ is reduced matrix with rank t,

α and α' are quantum numbers for J and J' states, respectively

  - determine radiative transition probability, A_{rad} for $J \rightarrow J'$ transition

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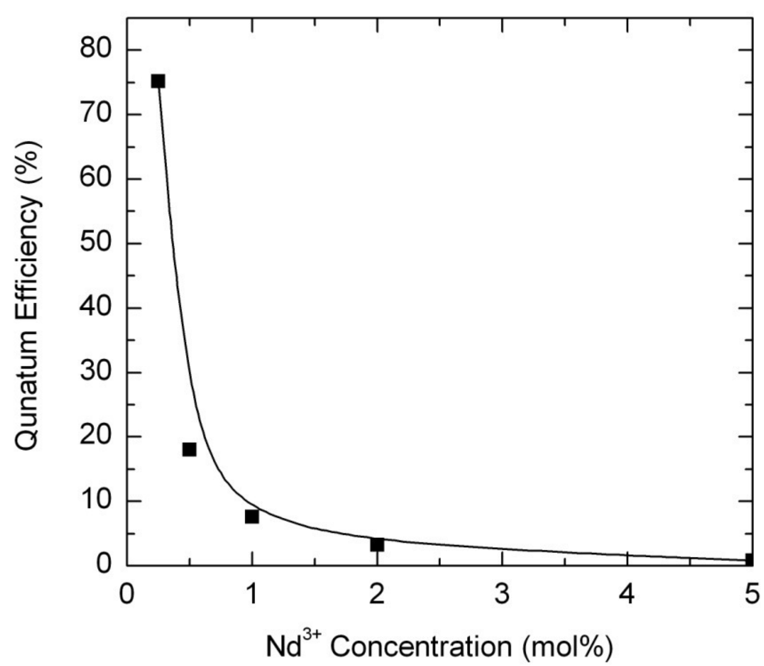
Quantum Efficiency of YF_3:Nd

- Quantum efficiency, η : percent photons emitted from desired transition

$$\eta = \frac{\Sigma A_{rad,i}}{\Sigma A_{rad,i} + \Sigma A_{non-rad}} = \frac{\tau_{lum}}{\tau_{rad}} \quad \text{and} \quad \Sigma A_{non-rad} = A_{ET} + A_{MPR} + A_{OH}$$

A_{ET} : losses from energy transfer (mainly dipole-dipole, dep. on RE-ion spacing)
A_{MPR} : multiphonon relaxation losses (surface defects, traps)
A_{OH} : losses from –OH quenching



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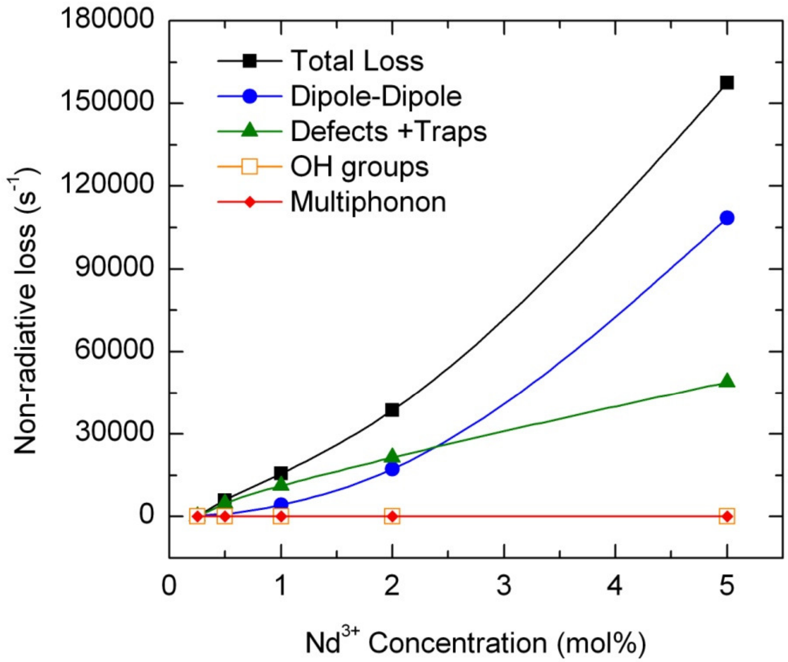
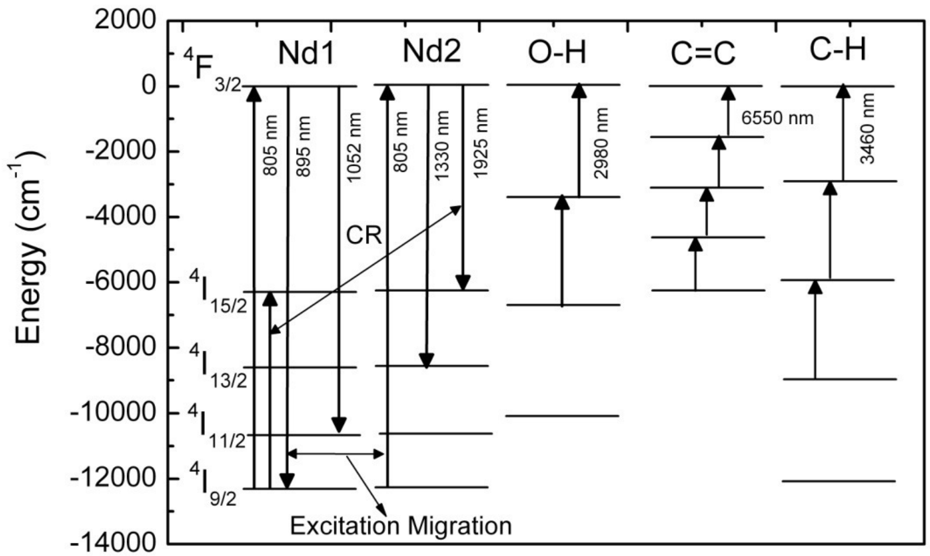
Non-Radiative Losses of YF_3:Nd



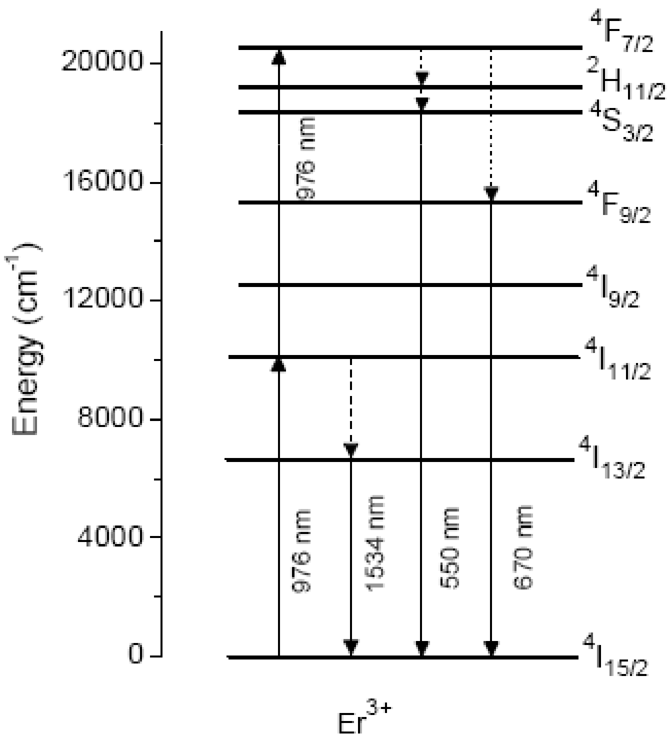


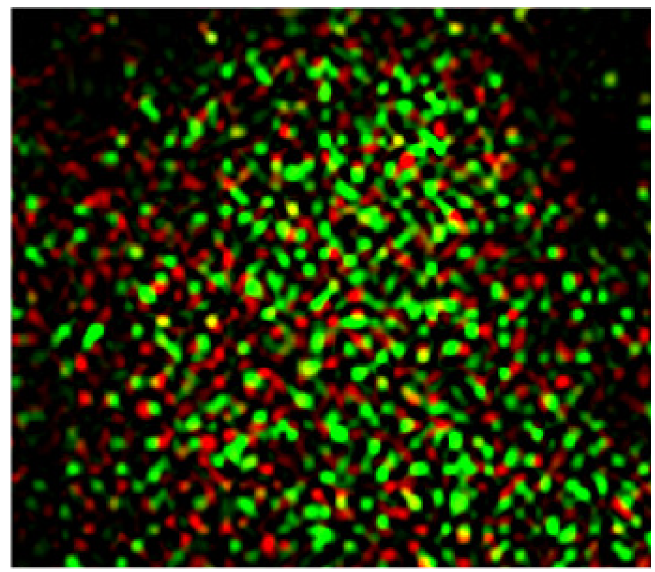
- Dipole-dipole interactions dominate non-radiative losses
- C-H resulted in reduced efficiency of 1052 nm emission
- O-H, C=C and C-H quenchers of 1925 nm emission

Other Losses → Upconversion!

- Despite reducing non-radiative losses, infrared-to-visible upconversion reduces intensity of IR emission

Typical halide hosts
(e.g. $NaYF_4$)





Q Wang, MC Tan, R Zhuo, GA Kumar, RE Riman, J. Nanosci. Nanotech., *in press*.

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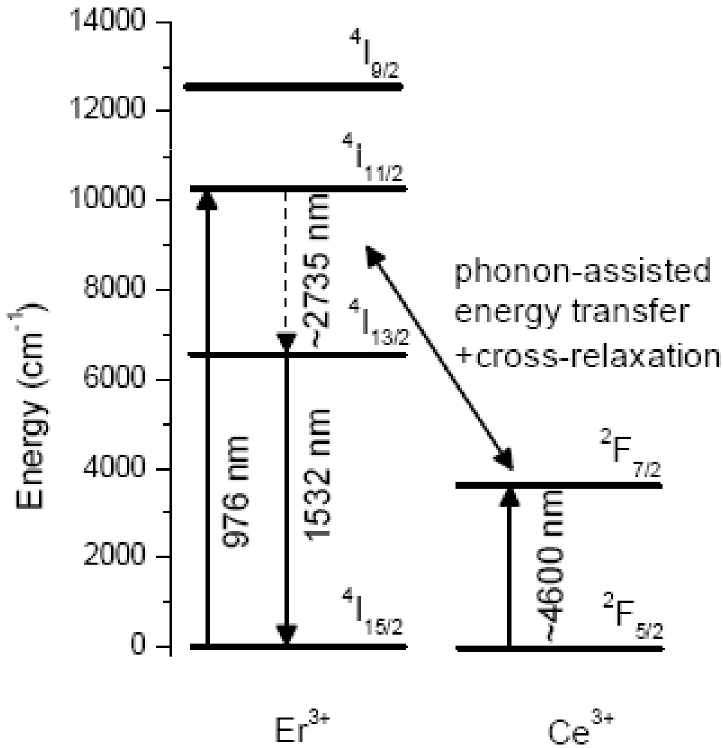
IR Emission Without Upconversion

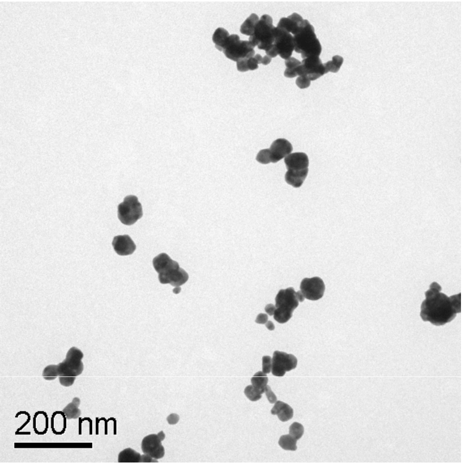
- Rare earths doped within interactive CeF_3 host enabled intense IR emission without upconversion

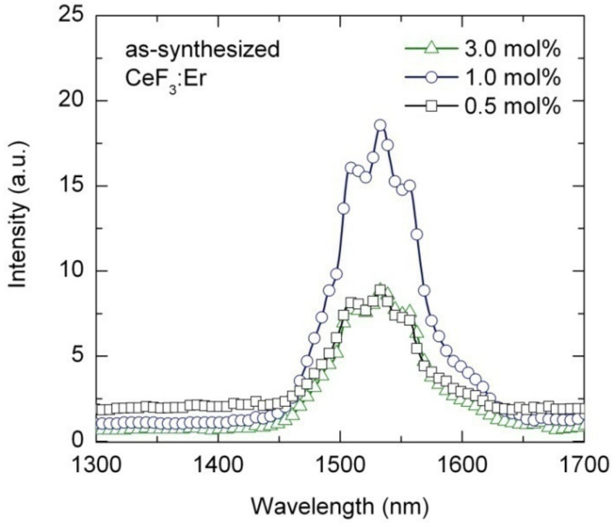


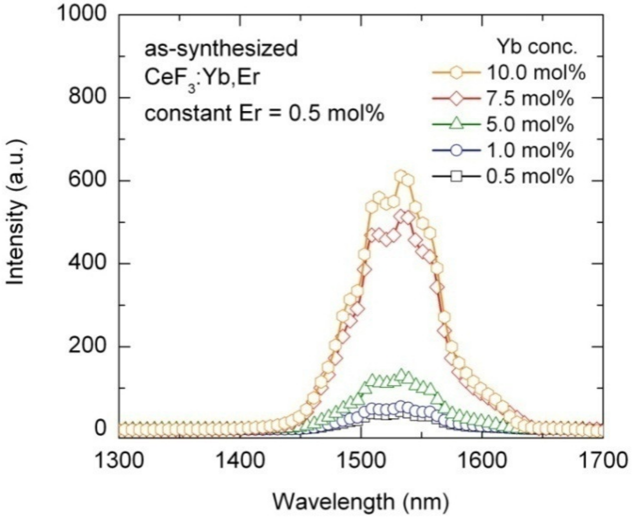
RE. Riman, MC Tan, GA Kumar, US Provisional Patent, Application Number 61139264 (2008).

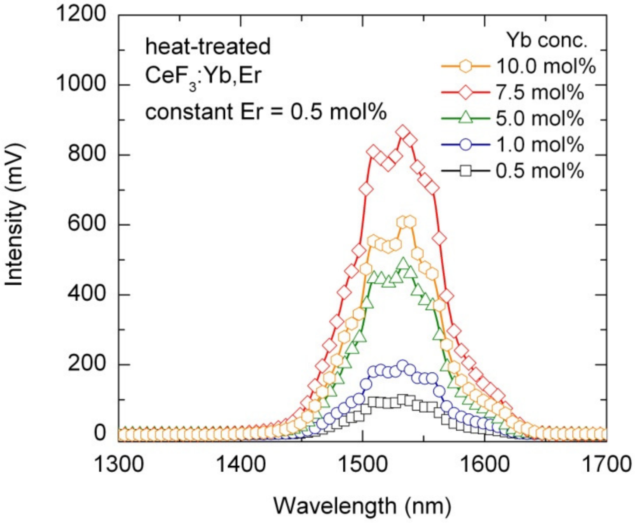
Er & Yb-Er Doped CeF_3 Nanoparticles

- Intense IR emission-no visible emission!
  - 980 nm excitation light source
  - Increased IR branching ratio via phonon-assisted energy transfer to Ce^{3+}
  - Yb co-doping increased 980 nm absorption efficiency, resulting in ~25X increase in emission intensity
  - Further increase in emission (~2 times) after heat treatment









MC Tan, GA Kumar, RE Riman, Opt. Express, *in press*.

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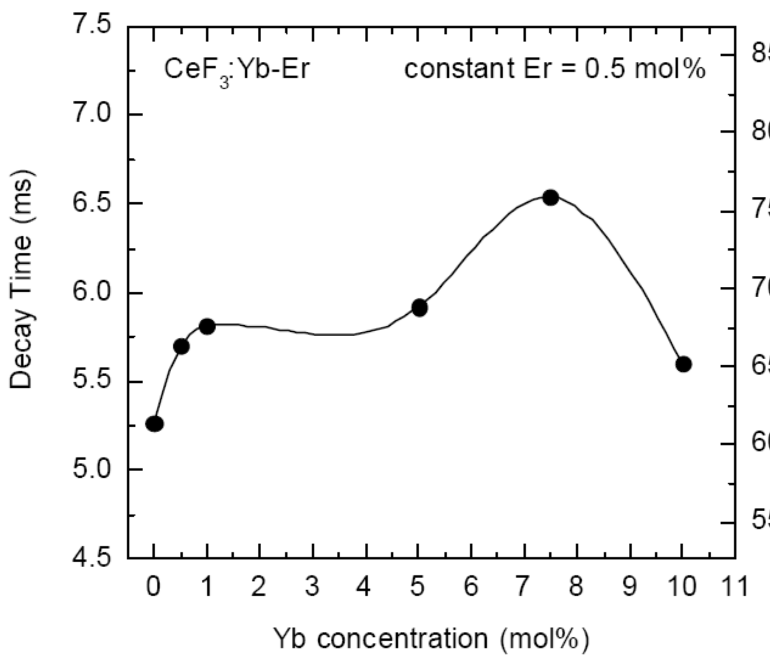
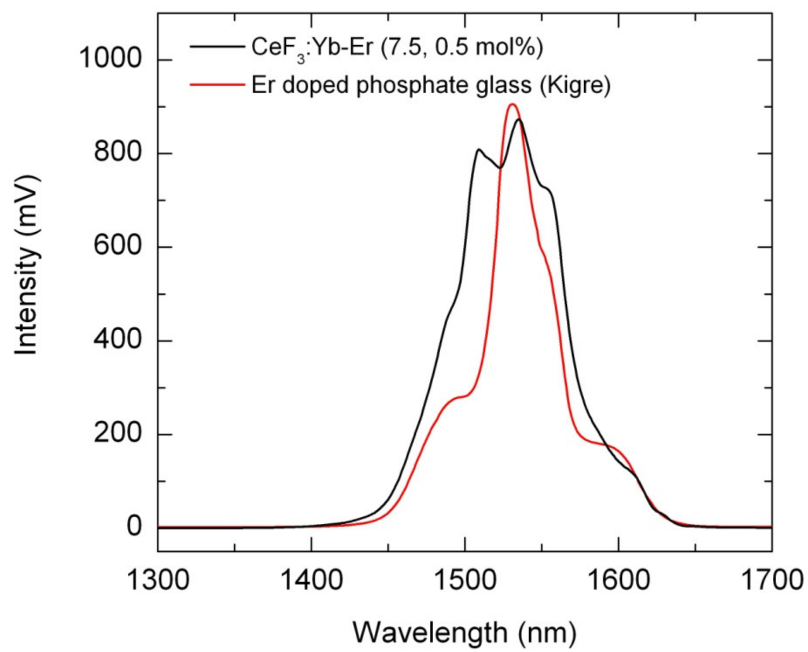
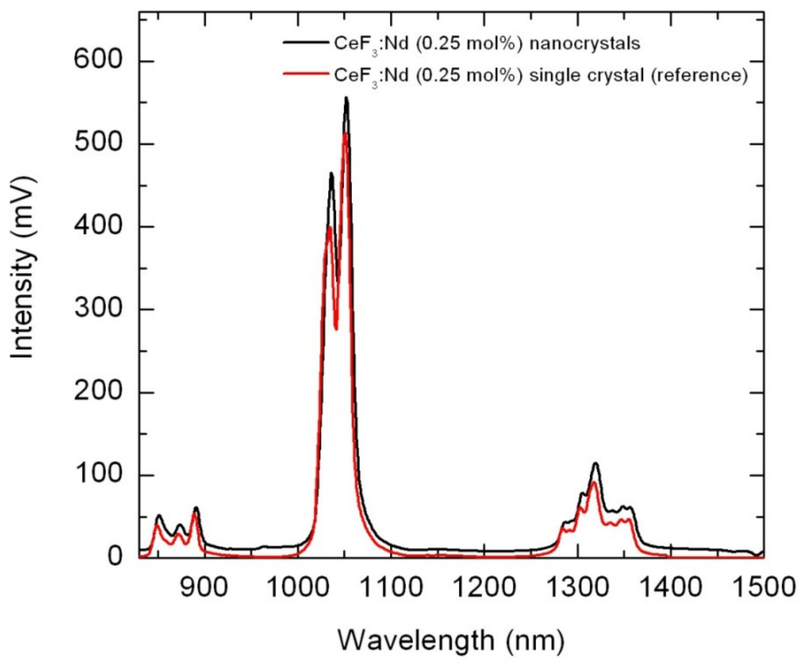
Comparison with Commercial Laser Glass

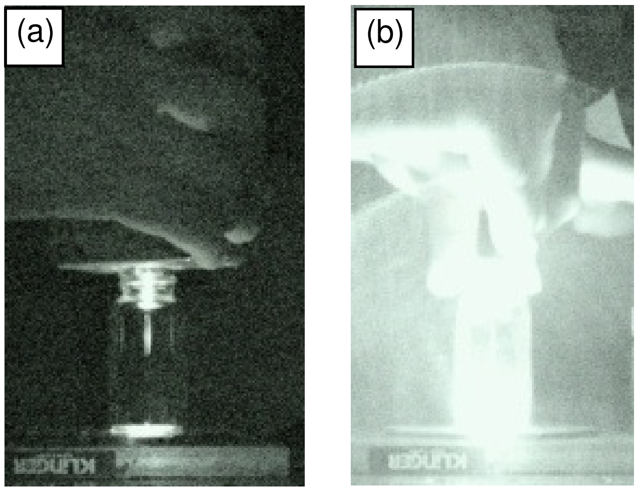
- Er-doped phosphate laser glass (Kigre Inc., South Carolina)
- Glass up-converts, difficult to make and is very expensive
- Our emission properties match those of the world's best Er-doped glass!
  - CeF_3:Yb-Er: Max. intensity ~870 mV and decay time ~6.5 ms
  - Kigre Glass: Max. intensity ~900 mV and decay time ~8 ms





Nd- and Pr- doped CeF_3 Nanoparticles





(a) Background (empty vial)
(b) Powder emission using handheld laser

- No visible emisisons from upconversion observed
- CeF_3:Nd nanoparticles as bright as its standard bulk single crystal
- Emission from CeF_3:Pr nanoparticles easily captured using commercial night vision camera

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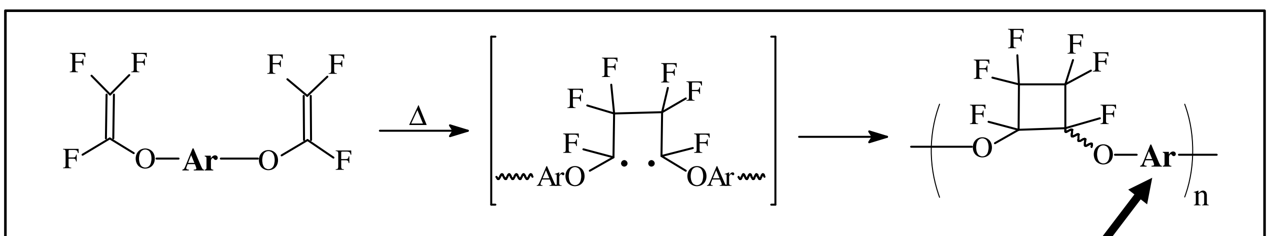
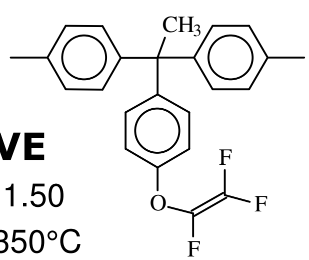
Polymers Selection

- Replace –CH and –OH groups to prevent quenching
- Suitable candidates:
  - Fluoracrylates (Allied Chemical), Teflon AF (Dupont), Ultradel (Amoco), CYTOP (Asahi Chemical), PFCB (Tetramer Technologies, Inc.)
- Most are costly and difficult to process (e.g. Teflon AF)
- Selecting PFCB

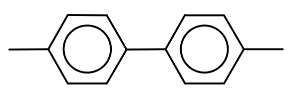


Perfluorocyclobutyl (PFCB) ring

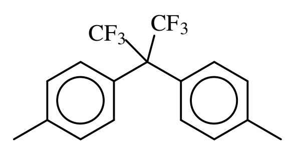
For **Ar** =



TVE
n ~ 1.50
T_g ~ 350°C

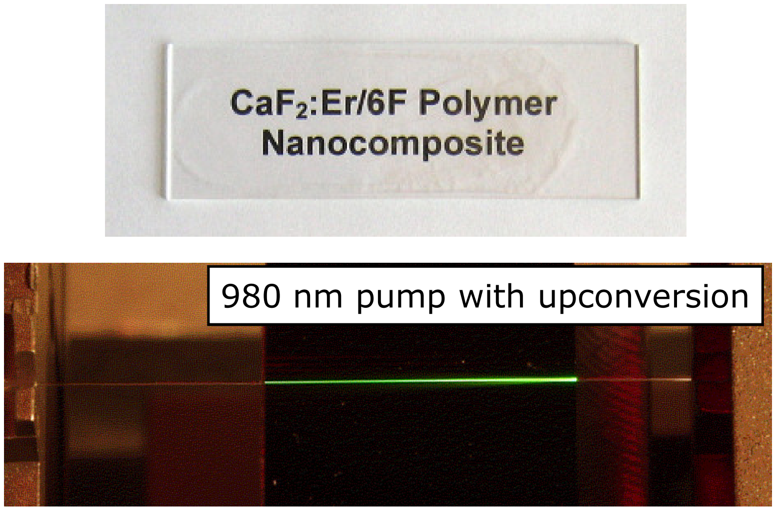


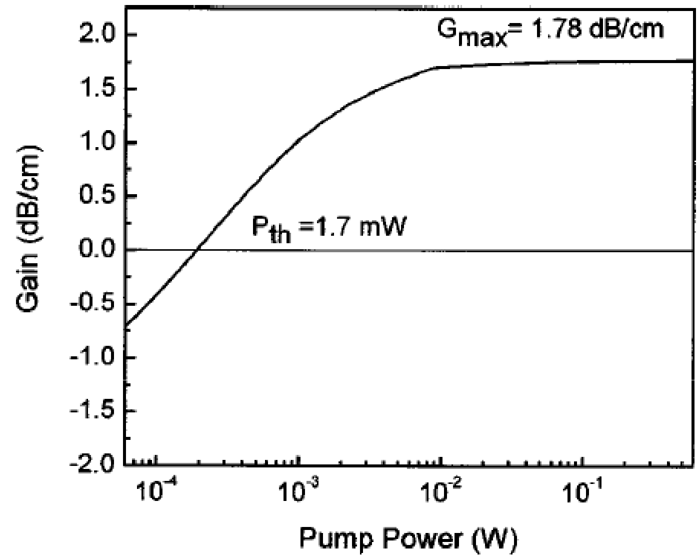
BPVE
n ~ 1.54
T_g ~ 250°C



6F
n ~ 1.44
T_g ~ 120°C

CaF_2:Er Fluoropolymer Nanocomposites



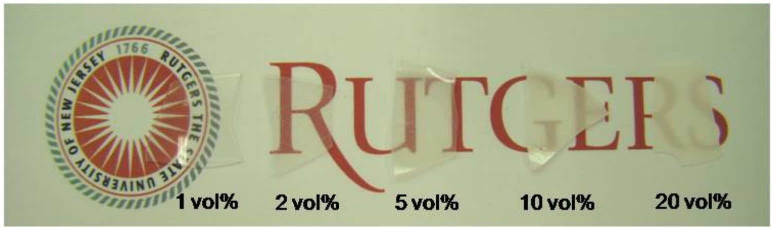


- Transparent CaF_2:Er/6F fluoropolymer composites showed IR emission together with visible upconversion
- Predicted maximum gain of 1.78 dB/cm
- Potential applications as waveguides and optical amplifiers

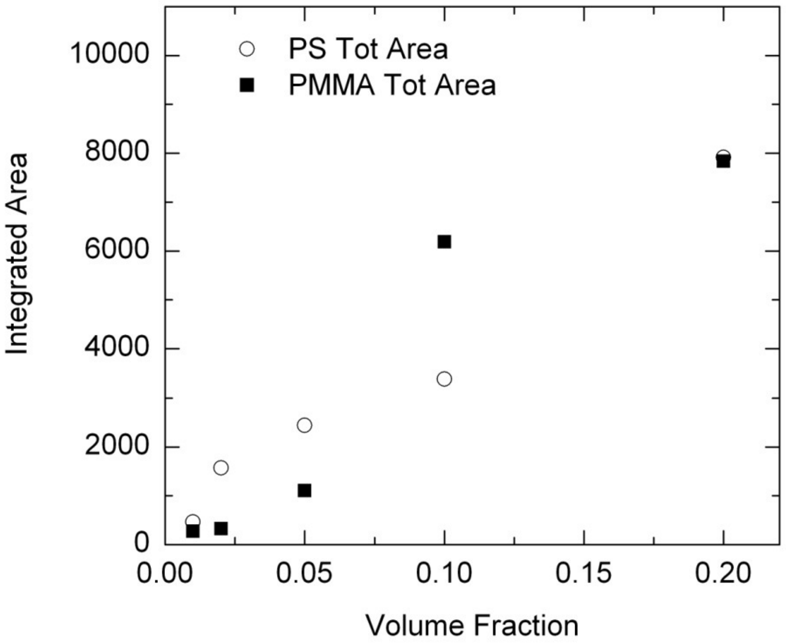
GA Kumar, CW Chen, RE Riman, S. Chen, D. Smith, J. Ballato, Appl. Phys. Lett., 86:241105 (2005) .

Transparent IR-emitting Nanocomposites

Polymethyl methacrylate nanocomposites



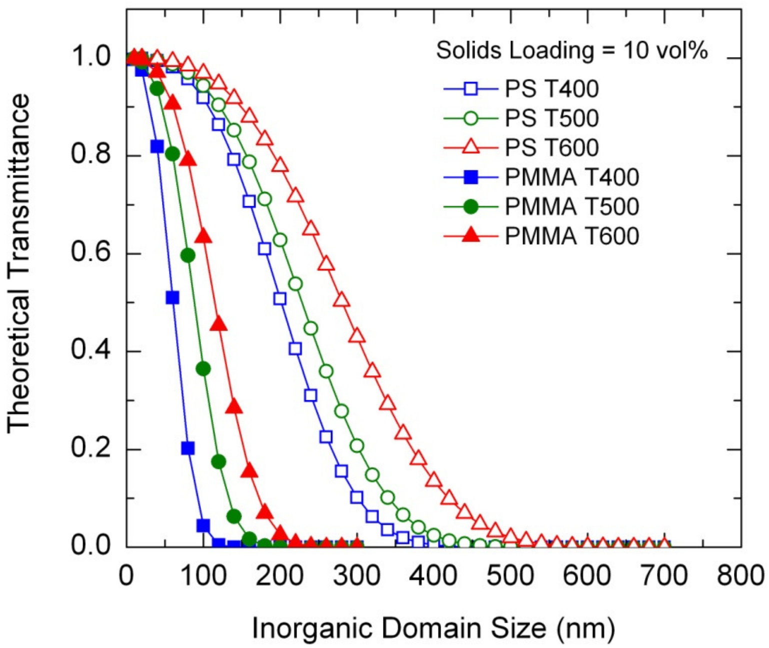
Polystyrene nanocomposites

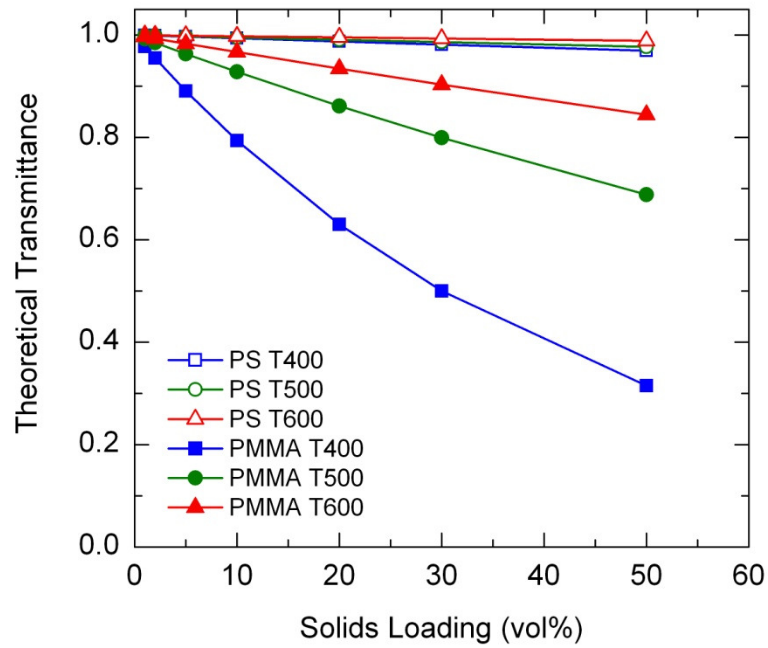


- Used low cost commodity polymers
  - Polymethyl methacrylate (PMMA) and Polystyrene (PS)
- Obtained transparent composites of rare-earth doped CeF_3 nanoparticles with high solid loading

MC Tan, SD Patil, RE Riman, *in preparation*.

Index Matching!

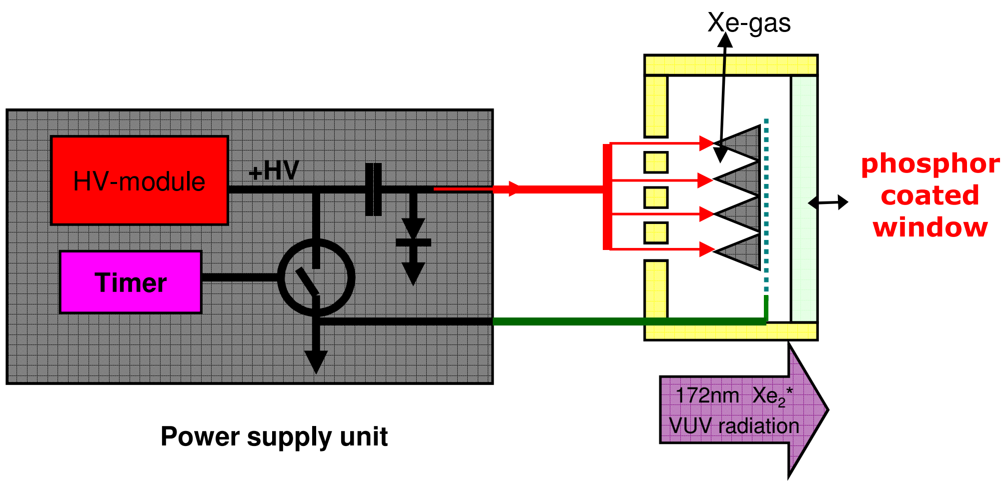




- At 1.5 µm, n_{PS}~ 1.57, n_{PMMA}~1.48; n_{part}~1.60
  - Δn (Particle:PMMA) ~ 0.12; Δn (Particle:PS) ~ 0.03
- Index matching allows more tolerance to dispersion quality(agglomerates, solid loading)

Phosphors for Efficient Hg-free Lighting

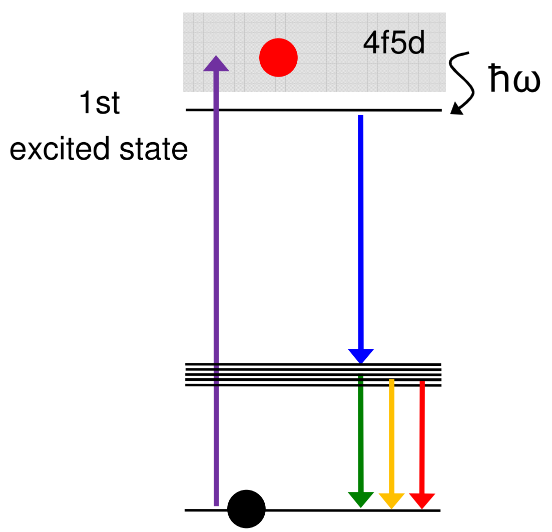
- Xe_2 excimer source (emission at 172 nm) and quantum cutting downconversion rare-earth halides
- Potential quantum efficiency at 200% with ~30% output
- Limitations to overcome:
  - light output (lumens/W) of Xe_2 lamps lower than Hg lamps
  - quantum cutting phosphor with high energy efficiency for VUV conversion by minimizing large losses by nonradiative relaxation



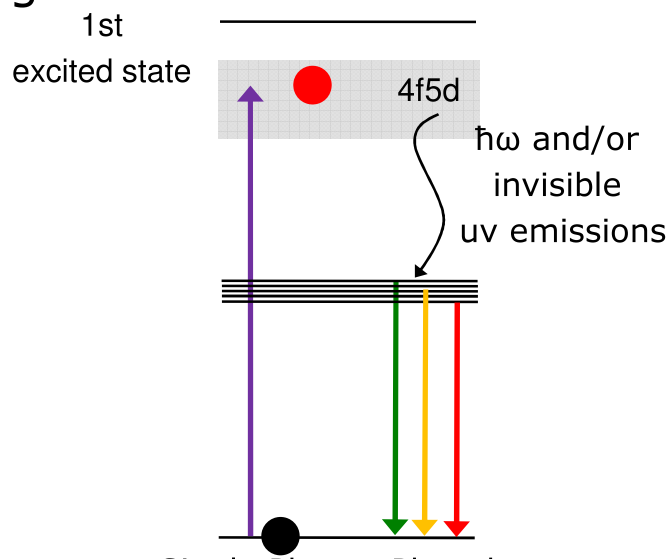
Schematic Courtesy of UV Solutions

Quantum Cutting Phosphors

- Emits >1 photons for each absorbed photon
- Max. potential quantum efficiency >100%
- Basic requirements
  - Energy band gap of the material E_g> 7eV
  - First excited state should lie below the 4f5d state
  - Low non-radiative loss which reduces the emission intensity
  - Strong absorption at the exciting radiation



Quantum Cutting Phosphor
e.g. YF_3:Pr



Single Photon Phosphor
e.g. $LaCl_3$:Pr

Green Quantum Cutting Phosphor